THE APPLICATION OF THE FERMI-THOMAS STATISTICAL MODEL TO THE CALCULATION OF POTENTIAL DISTRIBUTION IN POSITIVE IONS

BY EDWARD B. BAKER
Department of Physics, University of Michigan

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Abstract

The statistical method of Fermi and Thomas of calculating atomic potential distributions has been extended to include positive ions. A table of potentials for any positive ion is given. The results have been applied to the calculation of (a) ionic radii, (b) successive ionization potentials, (c) deviations from the Mosely law in optical spectra.

I. The Theory

FERMI[1] and Thomas[2] have considered the electrons in a neutral atom as a completely degenerate electron gas under the influence of the Coulomb field of the nucleus. Assuming radial symmetry, and using Poisson's equation, the Fermi-Dirac statistics permitted a calculation of the distribution of potential for neutral atoms. The present work provides a generalization of the method to include all positive ions also.

Fermi and Thomas obtained the differential equation

$$\frac{1}{r}\frac{d}{dr}\left(\frac{1}{r}\frac{dv}{dr}\right) = -4\pi\rho = \frac{2^{13/2}\pi^2 m^{3/2} e^{5/2}}{3h^3} v^{3/2} \tag{1}$$

with the boundary conditions

$$v \sim Ze/r \text{ near } r = 0, \text{ or } \lim_{r\to 0} vr = Ze \tag{2.0}$$

$$v(\infty) = 0 \tag{2.1}$$

which determine the solution for the neutral atom uniquely. The additional condition

$$\int \rho d\tau = -Ze \tag{3}$$

is simultaneously satisfied.

Introducing dimensionless variables

$$\psi = v/\gamma; \quad \gamma = \frac{2^{13/3}\pi^{4/3} m e^3 Z^{4/3}}{3^{2/3} h^2} \tag{4}$$

[1] E. Fermi, Zeits. f. Physik **48**, 73 (1928).
[2] L. H. Thomas, Proc. Camb. Phil. Soc. **23**, 542 (1927).

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and

$$x = r/\mu; \qquad \mu = \frac{3^{2/3}h^2}{2^{13/3}\pi^{4/3}me^2Z^{1/3}}$$

then Eq. (1) becomes

$$\frac{d^2\psi}{dx^2} + \frac{2}{x}\frac{d\psi}{dx} = \psi^{3/2} \tag{5}$$

Substituting $\phi = \psi x$, we have

$$\phi'' = \frac{\phi^{3/2}}{x^{1/2}} \tag{6}$$

and Eqs. (2) and (3) become

$$\phi(0) = 1 \tag{7}$$

$$\phi(\infty) = 0 \tag{7.1}$$

and

$$\int_0^\infty \phi^{3/2}(x)^{1/2}dx = 1. \tag{8}$$

For the positive ion having z electrons and the atomic number Z, which we shall call an ion of order σ ($\sigma = z/Z$), we have, in place of Eq. (3),

$$\int \rho d\tau = -ze \tag{9}$$

and, in place of Eq. (8),

$$\int_0^{x_m} \phi^{3/2}x^{1/2}dx = z/Z = \sigma. \tag{10}$$

Since Eq. (9) is not fulfilled by the former solution, it follows that the boundary condition, Eq. (2.1), must be modified, since Eq. (2.0) must remain the same. A suggestion of how this is to be done may be obtained by a comparison of Eq. (5) with the equations

$$\frac{d^2\psi}{dx^2} + \frac{2}{x}\frac{d\psi}{dx} = -\psi^n \tag{11}$$

which have been extensively studied by Emden[3] in connection with the distribution of matter in polytropic gas spheres. Emden found that for certain values of n, and certain boundary conditions, there are solutions of Eqs. (11) describing gas spheres of *finite* radius. This suggests that Eq. (3) may also have such solutions if the boundary conditions are modified.

Fermi[4] and Razetti[5] have used the approximate potential

$$v = -\frac{e}{r}\left[1 + (Z-1)\phi\left(\frac{r}{\mu}\right)\right] \tag{12}$$

[3] Emden, "Gaskugeln," Leipzig, 1907.
[4] E. Fermi, Zeits. f. Physik **49**, 550 (1928).
[5] F. Razetti, Zeits. f. Physik **49**, 546 (1928).

(where μ is evaluated for $Z-1$), for a singly ionized atom. This is obtained by considering the ion of nuclear charge Z as a neutral atom of nuclear charge $Z-1$ plus an extra proton in the nucleus. This approximation neglects the "packing effect" that the added proton will have upon the electron cloud. It is not possible to generalize this result for much higher ionizations, for then the neglect of the packing effect becomes serious. The present method is designed to remove this difficulty.[6]

We propose a model of the positive ion having a finite radius x_m, beyond which the charge density is zero. The solution ϕ_σ of Eq. (6), representing a positive ion of order σ, must obey the boundary condition

$$\phi_\sigma(x_m) = \phi_{\sigma m} = 1 - \sigma = 1 - z/Z \tag{13}$$

instead of Eq. (7.1). We find that ϕ_σ then fulfills the extra condition of Eq. (10). For the neutral atom $x_m = \infty$, Eq. (13) reduces to Eq. (7.1), and Eq. (10) reduces to Eq. (8), as required.

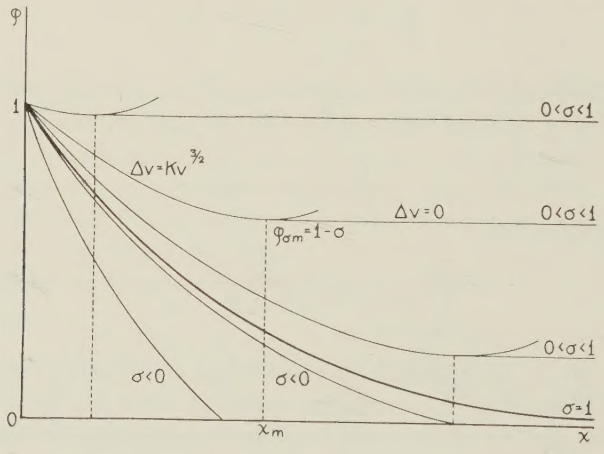

Fig. 1.

In Fig. 1 are displayed the possible forms the solution of Eq. (6) may take if the boundary condition of Eq. (7.0) is satisfied. The curve ϕ_1 is the only solution for which $\phi(\infty)=0$, and is that already obtained for the neutral

[6] The two dimensional analogue of Eq. (5) is

$$\frac{d^2\psi}{dx^2} + \frac{1}{x}\frac{d\psi}{dx} = \psi$$

the solution of which is any cylinder function $Z_0(ix)$. The only cylinder function which has the required logarithmic behavior for $x=0$, and which vanishes for $x=\infty$, is the Hankel function of the first kind $H_0^1(ix)$. As this function becomes asymptotically equal to $e^{-x}/x^{\frac{1}{2}}$, it can only represent a neutral two dimensional atom. The corresponding fact is true for Eq. (5); there is no solution of Eq. (5) which satisfies the conditions of Eqs. (2.0) and (2.1) other than the one obtained by Thomas and Fermi for neutral atoms. This can also be shown by a direct method of inequalities. This remarkable property of Eq. (5) made necessary the linking up of two solutions as described above.

atom by Fermi and Thomas. For this solution we have found the starting slope $\phi_1'(0) = -B_1 = -1.588558$.

Since the differential equation is of the second order, a particular value of the initial slope $-B_\sigma$ at $x=0$ uniquely determines a single solution passing

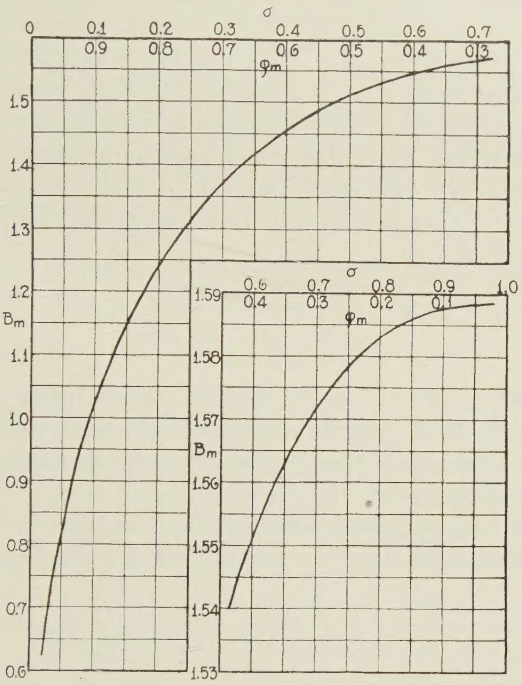

Fig. 2.

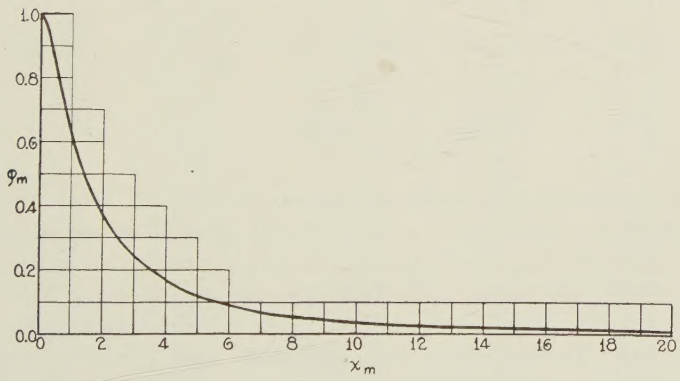

Fig. 3.

through $\phi=1$, $x=0$. All solutions with $0 > -B_\sigma > -\infty$ are single valued in ϕ, and no two cross each other.

All solutions with $0 > -B_\sigma > -B_1$ have each a single minimum, the coordinates of which $(\phi_{\sigma m}, x_m)$ are monotonous functions of B_σ (see Fig. 2), so that

the locus of minima (see Fig. 3) is monotonous in both x and ϕ. The ordinates at the minimum range from $\phi_{1m}=0$ to $\phi_{\sigma m}=1$, for values of B_σ from B_1 to B_0 respectively. These solutions describe any positive ion ($0\leqq\sigma\leqq 1$) as far as the minimum, which is the boundary of the ion; beyond that point the Coulomb field requires a straight line parallel to $\phi=0$, and a distance $1-\sigma$ above it, corresponding to a solution of Laplace's equation, which joins at the minimum a solution ϕ_σ of Eq. (8). The value of σ which belongs to a solution ϕ_σ, having a starting slope $-B_\sigma$, is thus *determined* by numerical integration from $\phi=1$, $x=0$, $\phi'=-B_\sigma$ to the minimum, and by there *assigning* the value $1-\sigma$ to the ordinate $\phi_{\sigma m}$. The value of σ is known to characterize the straight line $1-\sigma=\phi$, which is the solution of Laplace's equation for the region outside of an ion of order σ. This condition expresses the fact that the potential of a positive ion must be

$$v\sim\frac{(Z-z)e}{r}=\frac{Ze}{r}(1-\sigma)$$

for large values or r.

All solutions of Eq. (8) with $-B_1>-B_\sigma>-\infty$ lie below ϕ_1 and terminate abruptly at $\phi=0$, so that they do *not* represent negative ion distributions. Negative ions, as a matter of fact, will not find a place in any theory which assumes radial symmetry.

Since $x=0$, $\phi=1$ is a winding point with ϕ'' infinite, it is not possible to integrate from there using Taylor's series. Instead the expansions

$$\phi=1-Bx+\frac{4}{3}x^{3/2}-\frac{2}{5}Bx^{5/2}+\frac{1}{3}x^3+\frac{3}{70}B^2x^{7/2}-\frac{2}{15}Bx^4+\frac{4}{63}\left(\frac{2}{3}+\frac{1}{16}B^3\right)x^{9/2}+\cdots \tag{14}$$

and

$$\phi'=-B+2x^{1/2}-Bx^{3/2}+x^2+\frac{3}{20}B^2x^{5/2}-\frac{8}{15}Bx^3+\frac{2}{7}\left(\frac{2}{3}+\frac{1}{16}B^3\right)x^{7/2}+\cdots \tag{15}$$

obtained by a method of successive approximations, are used, since they are rapidly convergent near $\phi=1$, $x=0$. Starting with an arbitrary value of B_σ, the integration is carried out to the minimum by an extension of the method given by Whittaker and Robinson[7] for equations of the first order. The results must be given in a bivariate table, with values of ϕ for each value of x and B_σ or σ. This would be very extensive, were it not for the fact that, for each particular value of x, the values of both ϕ_σ and ϕ_σ', from one curve to another, depend linearly upon B_σ. By means of the formulae:

$$\phi_\sigma=k(B_\sigma-B_p)+\phi_p \tag{16}$$

$$\phi_\sigma'=k'(B_\sigma-B_p)+\phi_p' \tag{17}$$

[7] Whittaker and Robinson, "The Calculus of Observations."

and Table I, we may easily find the values of ϕ_σ and ϕ_σ' for each value of σ, at the values of x given in the table. For intermediate values linear interpolation is sufficiently accurate. The constants k and k', being functions of x, are also tabulated, as well as the values B_p, ϕ_p and ϕ_p' of the reference solutions. The values of $B_{\sigma m}$ and $\phi_{\sigma m}$ are also listed; they are the initial slopes and minimal ordinates, respectively, of the solutions having their minima at the given value of x. Since $\phi_{\sigma m} = 1 - \sigma$, this part of the table is used to find the initial slope B_σ, needed in Eqs. (16) and (17), corresponding to the given order σ of the ion. This may also be done using Fig. 2. In Fig. 3 values of $\phi_{\sigma m}$ are plotted against x_m, and from this, since $\phi_{\sigma m} = 1 - \sigma$, we may find the radius x_m of an ion of order σ.

Values are listed from $x = 0.10$ to $X = 14.88$. For values of $x < 0.10$ the series in Eqs. (14) and (15) may be used.

II. Ionic Radii

Herzfeld[8] has given a summary of some fourteen different methods of determining ionic radii, most of which are experimental, or semi-experimental. It may be seen from his collection of data, that the radius of any particular ion has a wide range of values, according to the method of determination. This uncertainty is not experimental, but lies in the variation of meaning of the radius with the method. It is consequently quite useless to

Table I.
$B_p = 1.60$.

x	ϕ_p	$-(\partial\phi/\partial x)_p$	$-k$	$-k'$	B_m	ϕ_m
0.10	0.880448	1.0077	0.10126	1.0306	0.62221	0.97950
0.11	0.870539	0.9826	0.11159	1.0362	0.65170	0.97636
0.12	0.860832	0.9587	0.12197	1.0410	0.67901	0.97316
0.13	0.851358	0.9362	0.13240	1.0449	0.70399	0.96999
0.14	0.842103	0.9151	0.14287	1.0511	0.72935	0.96650
0.15	0.833053	0.8948	0.15342	1.0548	0.75166	0.96320
0.16	0.824201	0.8758	0.16401	1.0610	0.77453	0.95958
0.17	0.815535	0.8576	0.17464	1.0665	0.79592	0.95597
0.18	0.807046	0.8402	0.18418	1.0728	0.81678	0.95130
0.20	0.790574	0.80745	0.20576	1.0861	0.85655	0.94355
0.22	0.774731	0.7772	0.22761	1.0985	0.89248	0.93577
0.24	0.759471	0.7492	0.24971	1.1115	0.92596	0.92779
0.26	0.744751	0.72315	0.27208	1.1255	0.95746	0.91957
0.28	0.730535	0.69875	0.29473	1.1391	0.98658	0.91133
0.30	0.716792	0.67585	0.31765	1.1540	1.01434	0.90283
0.32	0.703492	0.6544	0.34089	1.1698	1.04059	0.89419
0.34	0.690609	0.63415	0.36447	1.1856	1.06513	0.88556
0.38	0.666003	0.5968	0.41251	1.2184	1.11013	0.86808
0.42	0.642812	0.5633	0.46193	1.2523	1.15018	0.85060
0.46	0.620895	0.5330	0.51275	1.2887	1.18639	0.83298
0.50	0.600134	0.50545	0.56505	1.3264	1.21892	0.81546
0.54	0.580427	0.4803	0.61888	1.3659	1.24839	0.79804
0.58	0.561684	0.4572	0.67434	1.4069	1.27500	0.78084
0.62	0.543825	0.4360	0.73146	1.4492	1.29916	0.76388
0.66	0.526781	0.41645	0.79031	1.4935	1.32216	0.74715
0.74	0.49490	0.3816	0.91345	1.5882	1.35972	0.71444
0.82	0.46561	0.35125	1.0443	1.6851	1.39155	0.68329
0.90	0.43858	0.3250	1.1833	1.7913	1.41856	0.65326
0.98	0.41352	0.30225	1.3310	1.9052	1.44136	0.62467

[8] K. F. Herzfeld, Jahrb. der Radioakt. und Electronik **19**, 259 (1922).

TABLE I. (*continued*)

x	ϕ_p	$-(\partial\phi/\partial x)_p$	$-k$	$-k'$	B_m	ϕ_m
1.06	0.39017	0.2819	1.4882	2.0239	1.46072	0.59744
1.14	0.36836	0.2639	1.6551	2.1502	1.47728	0.57148
1.22	0.34789	0.24825	1.8325	2.2866	1.49143	0.54684
1.30	0.32859	0.2341	2.0212	2.4293	1.50362	0.52339
1.38	0.31037	0.22175	2.2216	2.5827	1.51414	0.50112
1.46	0.29308	0.21075	2.4347	2.7470	1.52328	0.47987
1.54	0.27662	0.2006	2.6612	2.9547	1.53210	0.45732
			$B_p=1.589$			
1.649	0.28827	0.1546	2.9889	3.1213	1.53939	0.43653
1.822	0.26312	0.1361	3.5600	3.4885	1.55001	0.40192
2.014	0.23878	0.1186	4.2678	3.906	1.55863	0.36839
2.226	0.21538	0.1027	5.149	4.408	1.56569	0.33540
2.460	0.19305	0.08866	6.250	5.027	1.57136	0.30327
2.718	0.17180	0.07616	7.649	5.764	1.57579	0.27286
3.004	0.15167	0.06515	9.367	6.572	1.579133	0.24410
3.320	0.13266	0.05560	11.62	7.701	1.581780	0.21656
3.669	0.11472	0.04748	14.38	9.085	1.583774	0.18986
4.055	0.09776	0.04069	18.21	10.79	1.585230	0.16640
4.482	0.08165	0.03512	23.26	12.74	1.586243	0.14577
4.953	0.06619	0.03081	30.11	15.32	1.586989	0.12673
5.474	0.05105	0.02758	38.90	18.56	1.587515	0.10883
6.050	0.03587	0.02537	50.63	22.61	1.587878	0.09268
			$B_p=1.5886$			
6.686	0.04672	0.01340	66.60	28.12	1.5881234	0.07846
7.389	0.03817	0.01108	88.40	34.24	1.5882763	0.06679
8.166	0.03029	0.00932	118.2	42.37	1.5883801	0.05629
9.025	0.02286	0.00806	159.3	53.19	1.5884485	0.04699
9.974	0.01565	0.00723	216.3	66.97	1.5884921	0.03900
			$B_p=1.58857$			
11.02	0.01716	0.00434	296.0	85.30	1.5885191	0.03218
12.18	0.01252	0.00373	408.0	107.6	1.5885353	0.02666
13.46	0.00802	0.00335	563.0	136.7	1.5885454	0.02182
14.88	0.00341	0.00319	782.0	171.4	1.5885514	0.01798

expect quantitative agreement of the radii determined by this theory, which themselves have little real meaning, with his values. Never-the-less, they do correspond in order of magnitude, and show the same general variation with atomic number. The class of ions considered by Herzfeld is a restricted class, having values of z equal to $Z-q$, where q is the valence of the element Z. When their radii are plotted against Z, a Lothar Meyer curve is obtained. We have made a similar curve, Fig. 4, of the values found from Fig. 3, but only for elements having positive ions.

III. Successive Ionization Potentials

Milne[9] has applied the Fermi-Thomas theory of the neutral atom to the calculation of the total potential necessary to remove all of the electrons from

[9] E. A. Milne, Proc. Camb. Phil. Soc. **23**, 794 (1927).

a neutral atom. Since our theory also gives a description of positive ions, the natural extension of the work of Milne is the calculation of the *successive* ionization potentials of atoms, or the successive potentials necessary to remove the electrons from an atom one at a time, further "stripping" the atom at each step.

The method of calculation consists in finding the total potential $X = X(\sigma, Z)$, necessary to remove all of the electrons from each kind of a positive ion that an element of atomic number Z may have, including the neutral atoms

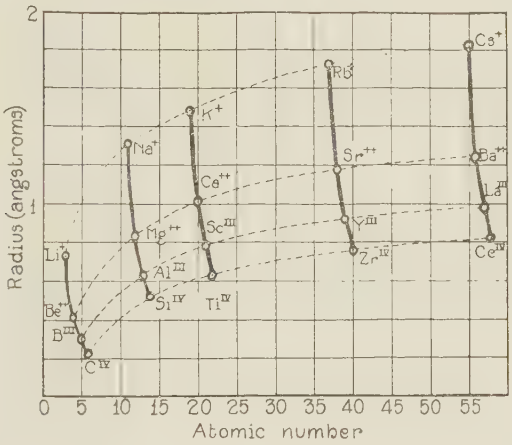

Fig. 4.

Successive differences of these quantities give the desired successive ionization potentials.

Milne considered the total electrostatic potential V to consist of two parts, Ze/r due to the nucleus, and $v(r)$ due to the charge cloud. At the nucleus $v(r)$ takes the constant value v_0, the "back potential" of the charge cloud, and this he showed proportional to the starting slope of ϕ_1, which is $-B_1$. There is a charge Ze at the nucleus, and at any other point a charge ρv. The total electrostatic potential is then

$$W = \Sigma \tfrac{1}{2} ev = \tfrac{1}{2} \int \rho v d\tau + \tfrac{1}{2} Z e v_0, \tag{18}$$

and the total energy is half of this.

The integral in the first term of Eq. (18) he showed to be proportional to B_1, which becomes B_σ for the ion. His result may be written:

$$X(1, Z) = -13.11 B_1 Z^{7/3} \text{ volts}. \tag{19}$$

He obtained his value of B_1 from Thomas' calculations of ϕ_1 near $x = 0$, which, however, are slightly in error. Using our value of $B_1 = -1.588558$, we obtain

$$X(1, Z) = 20.824 Z^{7/3} \text{ volts} \tag{20}$$

which does not agree as well with experiment as Milne's

$$X(1, Z) = 17Z^{7/3} \text{ volts}. \tag{21}$$

This agreement must be regarded as accidental.

For the positive ion of order σ we obtain

$$X(\sigma, Z) = -13.11B_\sigma Z^{7/3} \text{ volts}. \tag{22}$$

If the approximation of Fermi and Razetti is generalized for ions of any order we obtain

$$X_F(\sigma, Z) = -13.11B_1\frac{7}{13}\left(\frac{6}{7}\sigma + 1\right)Z^{7/3} \text{ volts}, \tag{23}$$

since z must be used for the evaluation of v in the first term of Eq. (18). In successive differences only the term in Eq. (23) containing σ gives a contribution.

Fig. 5. Successive ionization potentials of oxygen. $Z=8$. Circles represent Hartree's Values.

In Figs. 5 and 6 we have plotted such differences of $X(\partial, Z)$ for the elements oxygen and iron. The broken curves are the semi-experimental values of Hartree.[10] As with most results of this statistical theory, a smooth curve

[10] D. R. Hartree, Proc. Camb. Phil. Soc. **22**, 473 (1924).

running through the jagged experimental one is obtained. Differences of X according to (23) give a curve of successive ionization potentials having a negative slope and going from the upper left hand corner to the lower right hand corner of the diagrams 5 and 6.

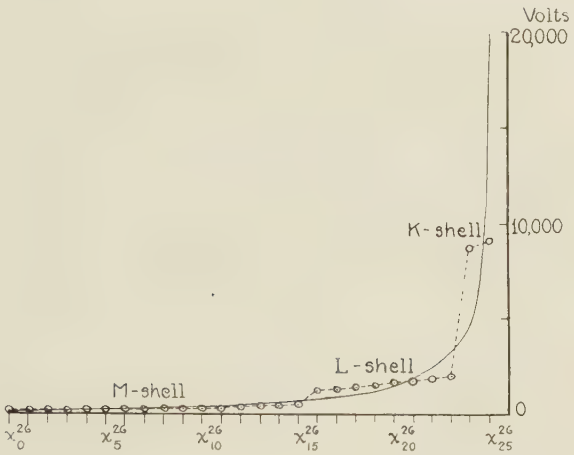

Fig. 6. Successive ionization potentials of iron. $Z=26$. Circles represent Hartree's values.

IV. Application to the Behavior of Optical Term Values in the Limit of Very High Frequencies

Sommerfeld has shown that x-ray terms may be represented by the semi-empirical term formula

$$-\frac{T}{R} = [Z/n - a(Z, n) - b(n, l)]^2 + \alpha^2\left[\frac{Z - d(n, l, j)}{n}\right]^4\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right) + \cdots \tag{24}$$

Laporte[11] has shown that this same formula may be used to represent optical terms, though the number $a(Z, n)$, which represents the screening of the outer electrons, is zero for optical terms, and $b(n, l)$ is a function of Z, except for very high ionizations ($\partial << 1$). For low ionizations its dependence upon Z may be expressed as the series

$$b(n, l, Z) = A(n, l) + \frac{B(n, l)}{Z} + \frac{C(n, l)}{Z^2} + \cdots \tag{25}$$

so that

$$\lim_{Z\to\infty} b(n, l, Z) = A(n, l). \tag{26}$$

It is possible to calculate the quantity $A(n, l)$, by means of the present theory, for hydrogenic ion series like Na I, Mg II, Al III, etc. It is also

[11] O. Laporte, "Sommerfeld Festschrift," Leipzig, 1928, p. 128.

possible to derive this from the experimental values of the line frequencies for such isoelectronic series. We shall be interested first in the latter problem.

Combining Eqs. (24) and (25) we have:

$$-\frac{T}{R}=\left\{\frac{Z}{n}-\left[A(n,l)+\frac{B(n,l)}{Z}+\frac{C(n,l)}{Z^2}+\cdots\right]\right\}^2 + \alpha^2\left\{\frac{Z-d(n,l,j)}{n}\right\}^4\left(\frac{n}{j+\frac{1}{2}}-\frac{3}{4}\right)+\cdots \tag{27}$$

Terms in α^2 and higher powers of α^2 represent the "relativity" correction, and if we subtract them from both sides of Eq. (27), we obtain the "reduced" term values t, thus

$$\begin{aligned}-\frac{t}{R}&=-\frac{T}{R}-\alpha^2\left\{\frac{Z-d(n,l,j)}{n}\right\}^4\left(\frac{n}{j+\frac{1}{2}}-\frac{3}{4}\right)+\cdots\\&=\left\{\frac{Z}{n}-\left[A(n,l)+\frac{B(n,l)}{Z}+\frac{C(n,l)}{Z^2}+\cdots\right]\right\}^2.\end{aligned} \tag{28}$$

We wish now to be able to calculate $A(n, l)$ from observed values of t. This may be done in at least two ways.

The first is to take the square root of the absolute values of both sides of Eq. (28), obtaining:

$$\left(\frac{t}{R}\right)^{1/2}=\frac{Z}{n}-A(n,l)-\frac{B(n,l)}{Z}-\frac{C(n,l)}{Z^2}+\cdots \tag{29}$$

which shows that the Moseley law holds for large values of Z. If we form the difference

$$\left(\frac{t(l_2)}{R}\right)^{1/2}-\left(\frac{t(l_1)}{R}\right)^{1/2}=[A(n,l_1)-A(n,l_2)]+\frac{1}{Z}[B(n,l_1)-B(n,l_2)] \tag{30}$$

and go to the limit for very large Z, we obtain the quantity

$$\lim_{Z\to\infty}\left\{\left(\frac{t(l_2)}{R}\right)^{1/2}-\left(\frac{t(l_1)}{R}\right)^{1/2}\right\}=[A(n,l_1)-A(n,l_2)]. \tag{31}$$

This quantity may be directly calculated from the experimental term values of an isoelectronic sequence, it being the asymptotic value that the quantities in Eq. (30) seem to approach for the heavier elements in the sequence. Such quantities have been calculated by Wentzel[12] and Unsöld,[13] on the basis of a model of the atomic core composed of concentric spherical surface charges. This quantity has the disadvantage that the absolute term values must be known in order to calculate it.

The second quantity which may be used as a medium of comparison of theory and experiment is the asymptotic value of the first differences, for

[12] G. Wentzel, Ann. d. Physik **76**, 803 (1925).

[13] A. Unsöld, Zeits. f. Physik **33**, 843 (1925).

neighboring elements in the isoelectronic sequence, of the line frequencies themselves. We may form this quantity from Eq. (28). It is

$$\lim_{Z\to\infty}\left\{\frac{\nu(l_2, l_1, Z+1)}{R} - \frac{\nu(l_2, l_1, Z)}{R}\right\}$$
$$= \lim_{Z\to\infty}\left\{\left[\frac{t(n, l_2, Z+1)}{R} - \frac{t(n, l_1, Z+1)}{R}\right] - \left[\frac{t(n, l_2, Z)}{R} - \frac{t(n, l_1, Z)}{R}\right]\right\} \qquad (32)$$
$$= \frac{2}{n}[A(n, l_1) - A(n, l_2)],$$

which is just $2/n$ times the quantity in Eq. (31).

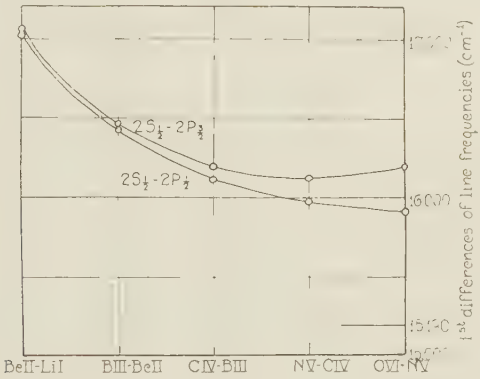

Fig. 7.

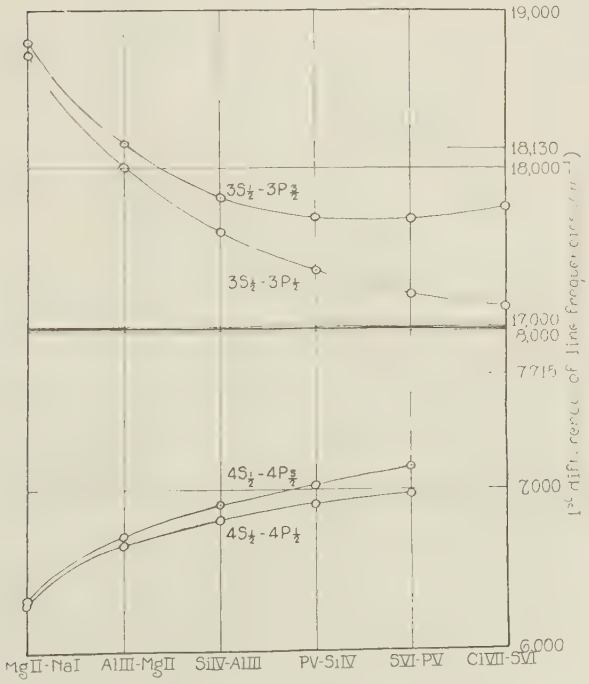

Fig. 8.

These two quantitites, in Eqs. (31) and (32), have been calculated by means of this theory, and have been compared with the experimental values of Bowen and Millikan[14] for the series Na I, Mg II, etc., and Li I, Be II, etc. in Figs. 7, 8, 9, and 10.

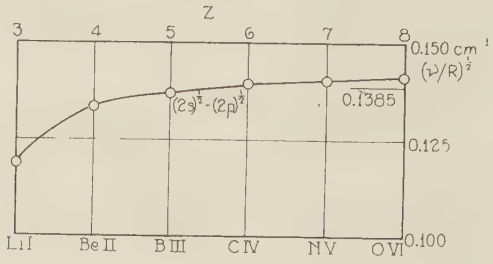

Fig. 9.

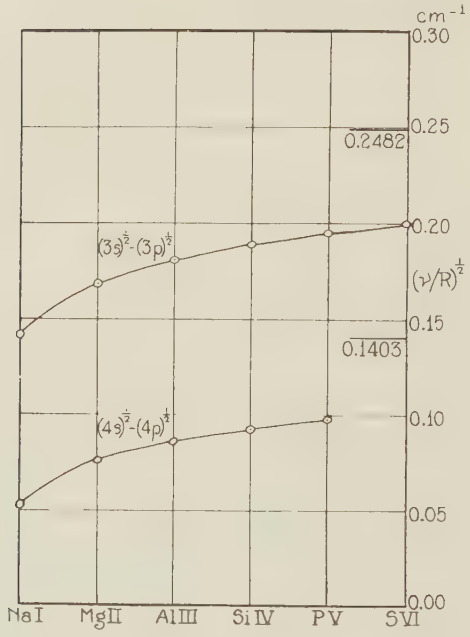

Fig. 10.

The use of the present theory to calculate these values involves the Schrödinger perturbation theory, since we are only interested in the energy values for large values of Z (σ nearly 0). We consider the core as a perturbation of an "hydrogenic" atom, writing the perturbation energy as

$$\epsilon = \frac{\int_0^\infty P(r)\psi^2 r^2 dr}{\int_0^\infty \psi^2 r^2 dr} \tag{33}$$

[14] I. S. Bowen and R. A. Millikan, Phys. Rev. **25**, 299 (1925), **27**, 145 (1926).

where ψ is the wave function of the unperturbed hydrogenic atom, and $P(r)$ is the perturbation function of the core. We proceed to construct $P(r)$.

Consider an ion of nuclear charge Z, with z electrons in the core, and one valence electron in addition. The potential energy of the valence electron in the field of the nucleus plus core is

$$-\frac{Ze^2}{r}\phi_\sigma\left(\frac{r}{\mu}\right) \tag{34}$$

where ϕ_σ is the generalized Fermi function for an ion of order σ. The net charge of the ion is $(Z-z-1)$.

The potential energy of the valence electron in the field of the nucleus alone (of charge Ze) is

$$-\frac{Ze^2}{r}. \tag{35}$$

If we add and subtract Eq. (35) to Eq. (34), we still have the potential energy of the valence electron in the field of the nucleus plus core as

$$-\frac{Ze^2}{r}+\frac{Ze^2}{r}\left[1-\phi_\sigma\left(\frac{r}{\mu}\right)\right]=-\frac{Ze^2}{r}+\Phi. \tag{36}$$

The quantity $\Phi=Ze^2/r[1-\phi_\sigma]$ may be split into two parts Φ_1 and Φ_2, such that

$$\Phi = \Phi_1 \text{ for } r \leqq r_m$$

$$\Phi = \Phi_2 \text{ for } r \geqq r_m,$$

where r_m is the radius of the core. If $r>r_m$, then

$$\phi_\sigma = \phi_{\sigma m} = 1 - \sigma = 1 - z/Z,$$

so that

$$\Phi_2 = \frac{Ze^2}{r}(1 - 1 + z/Z) = \frac{ze^2}{r}. \tag{37}$$

We may rewrite Eq. (36) in the form

$$-\frac{(Z-z)e^2}{r}+P(r) \tag{38}$$

where P is a function defined by

$$\begin{aligned} P &= \Phi_1 - Ze^2r \text{ for } r < r_m \\ P &= 0 \qquad\quad \text{for } r > r_m. \end{aligned} \tag{39}$$

Now, if Z is very large, we may think of the valence electron as being primarily in the field of a point charge $(Z-z)e$, and then being perturbed by

another system, with the perturbation energy $P(r)$. So, without the perturbation we have an hydrogenic atom with nuclear charge $(Z-z)e$ (i.e. the quantity z is the first approximation to the screening number $b(n, l, Z)$).

If $Z>>z$ (σ nearly 0), we may use the series approximation of ϕ_σ given in Eq. (14), since x_m is also nearly zero. By means of the analytical expressions of Eqs. (14) and (15) we are able to find an analytical expression for B_σ as a function of σ. To do this we notice that at the minimum

$$\phi' = 0 = -B + 2x_m^{1/2} - Bx_m^{3/2} + x_m^2 + \cdots . \tag{40}$$

Since both B and x_m are small, all terms after the first two are of lower order, so that, approximately,

$$B = 2x_m^{1/2};\ x_m^{1/2} = B/2;\ x_m = B^2/4. \tag{41}$$

Then, substituting in Eq. (14), we have

$$\begin{aligned} \phi_m = 1 - \sigma &= 1 - B(B^2/4) + \frac{4}{3}(B/2)^3 - \frac{2}{5}(B/2)^5 + \cdots \\ &= 1 - B^3/12 - B^6/80 + \cdots \end{aligned} \tag{42}$$

or, to the same approximation as in Eq. (41),

$$B^3/12 = \sigma;\ B = (12\sigma)^{1/3} \tag{43}$$

which is the required function. If we eliminate B from Eqs. (14) and (43), we obtain ϕ_σ in terms of x and σ explicitly. Thus

$$\phi_\sigma = 1 - (12\sigma)^{1/3}x + \frac{4}{3}x^{3/2} - \frac{2}{5}(12\sigma)^{1/3}x^{5/2} + \cdots \tag{44}$$

and therefore

$$\begin{aligned} \Phi_1 &= \frac{Ze^2}{r}\left[(12\sigma)^{1/3}x - \frac{4}{3}x^{3/2} + \frac{2}{5}(12\sigma)^{1/3}x^{5/2} + \cdots\right] \\ &= Ze^2\left[\frac{(12\sigma)^{1/3}}{\mu} - \frac{4}{3}\frac{r^{1/2}}{\mu^{3/2}} + \frac{2}{5}(12\sigma)^{1/3}\frac{r^{3/2}}{\mu^{5/2}} + \cdots\right]. \end{aligned} \tag{45}$$

Finally, we may write our perturbation function as

$$P(r) = Ze^2\left[\frac{(12\sigma)^{1/3}}{\mu} - \frac{4}{3}\frac{r^{1/2}}{\mu^{3/2}}\right] - \frac{ze^2}{r};\ r \leqq r_m \tag{46.0}$$

$$P(r) = 0;\ r \geqq r_m. \tag{46.1}$$

If we introduce the dimensionless variable

$$\rho = 2\frac{r}{r_0};\quad r_0 = \frac{r(Z-z)}{na_0}, \tag{47}$$

where Ze = the real nuclear charge

$(Z-z)e$ = the nuclear charge of our hypothetical hydrogenic atom

a_0 = the normal radius of the hydrogen atom

n = the principal quantum number,

we have the perturbation function

$$Q(\rho) = P(r) = a + b\rho^{1/2} + c/\rho, \tag{48}$$

with

$$a = \frac{Ze^2(12\sigma)^{1/3}}{\mu} = \left(\frac{Ze^2}{a_0}\right)\frac{8Z^{1/3}}{3^{1/3}\pi^{2/3}} \tag{49.0}$$

$$b = -\frac{4Ze^2}{3\mu^{3/2}}\left(\frac{a_0 n}{2(Z-z)}\right)^{1/2} = -\left(\frac{Ze^2}{a_0}\right)\frac{32n^{1/2}}{9\pi(1-\sigma)^{1/2}} \tag{49.1}$$

$$c = -\frac{2ze^2(Z-z)}{a_0 n} = -2\left(\frac{Ze^2}{a_0}\right)\left(\frac{1-\sigma}{n}\right) \tag{49.2}$$

$$\rho_m = 2\frac{r_m}{r_0} = \frac{2r_m(Z-z)}{na_0} = (1-\sigma)\frac{\pi^{2/3}3^{4/3}z^{2/3}}{4n} \tag{49.3}$$

and ϵ takes the form

$$\epsilon = \frac{\int_0^{\rho_m} Q(\rho)\psi^2(\rho)\rho^2 d\rho}{\int_0^{\infty} \psi^2(\rho)\rho^2 d\rho} \tag{50.0}$$

since $Q(\rho) = 0$ for $\rho \geqq \rho_m$.

The limiting forms of Eqs. (49) for $\sigma = 0$ are

$$b]_{\sigma=0} = -\left(\frac{Ze^2}{a_0}\right)\frac{32n^{1/2}}{9\pi} \tag{50.1}$$

$$c]_{\sigma=0} = -\frac{2}{n}\left(\frac{Ze^2}{a_0}\right) \tag{50.2}$$

$$\rho_m]_{\sigma=0} = \frac{\pi^{2/3}3^{4/3}z^{2/3}}{4n}. \tag{50.3}$$

We have passed to the limit several times during the process in order to simplify the calculations. The asymptotic form of the perturbation energy is

$$\epsilon_\infty = -L(n, l, z)\frac{Ze^2}{a_0} \tag{51}$$

If we were to extend the calculation for ϵ near the limit, we would find[1]

$$\epsilon = [-LZ + M + N/Z + \cdots]\frac{e^2}{a_0}. \tag{52}$$

The energy of the unperturbed hydrogenic ion, of nuclear charge $(Z-z)\ e$, is

$$E = -\frac{e^2(Z-z)^2}{2a_0 n} = -\frac{e^2}{2a_0 n}(Z^2 - 2zZ + z^2) \tag{53}$$

and therefore the sum

$$E_p = E + \epsilon = -\frac{e^2}{2a_0 n}[Z^2 - 2(Z - n^2L)Z + (z^2 - M) - N/Z + \cdots] \tag{54}$$

is the energy of the perturbed ion. From this the reduced term value is seen to be

$$-\frac{t}{R} = \frac{1}{n^2}[Z^2 - 2(z - n^2L)Z + (z^2 - M) - N/Z + \cdots] \tag{55}$$

In order to compare this with Eq. (28) we must place the square root of the right hand side under an indicated square. Thus

$$-\frac{t}{R} = \left\{\frac{Z}{n} - \frac{1}{n}(z - n^2L) - \frac{M - 2zn^2L - n^4L^2}{2Zn} + \cdots\right\}^2. \tag{56}$$

Comparing Eqs. (56) and (28) we may make the following identifications:

$$A(n, l) = \frac{1}{n}(z - n^2L) \tag{57.0}$$

$$B(n, l) = \frac{M - 2zn^2L - n^4L^2}{2n}, \text{ etc.} \tag{57.1}$$

From Eqs. (57.0) and (51) we may calculate quantitites such as those of Eqs. (30) and (31).

The quantitites of Eq. (30), which Wentzel introduced, must be calculated from "reduced" absolute term values. They are practically insensitive

[1] Since the perturbation function has the form of Eq. (48), the perturbation integrals reduce to sums of integrals of the type

$$I(\mu, \nu) = \int_0^\nu x^{\mu-1}e^{-x}dx$$

which are known as "incomplete Γ-functions." They are special cases of the "confluent hypergeometric functions." Tables of these functions have been prepared by K. Pearson ("The Incomplete Γ-function"), but interpolation is very laborious. However, since we encounter only whole or half integral values of μ, it is much simpler to reduce the integrals to polynomials (integral values), or to polynomials plus Gauss error functions, by partial integration.

to relativity corrections, but the absolute term values are only known by somewhat approximate calculations from line frequencies. The unreduced values of Bowen and Millikan are plotted in Figs. 9 and 10.

The quantitites calculated according to Eq. (31), though found directly from line frequencies, are very sensitive to relativity corrections, which are difficult to estimate accurately for s terms. Instead, in Figs. 7 and 8, the actual "unreduced" values are plotted for each of the doublet lines, to give an idea of the error involved in not reducing them. The lines on the right hand margin indicate the theoretical asymptotes.

In conclusion I wish to express my appreciation to Professor H. M. Randall, Director of the Physics department, for courtesies shown me during my graduate study at the University of Michigan. I am indebted to Professor O. Laporte for suggesting this problem to me, and for his constant advice. I also wish to thank Professors D. M. Dennison and E. A. Milne for valuable advice and criticism.